Soft synthesis of a metal-organic framework based on a tribarium building block

Bikshandarkoil R Srinivasan[a, *], Santosh Y Shetgaonkar[a] & Pallepogu Raghavaiah[b]

[a]Department of Chemistry, Goa University, Goa 403 206 India
Email: srini@unigoa.ac.in

[b]National Single Crystal X-ray Diffractometer Facility, School of Chemistry,
University of Hyderabad, Hyderabad 500 046 India

Reaction of MCO_3 (M = Ba or Ca) with benzene-1,3,5-tricarboxylic acid (H_3btc) in aqueous medium at room temperature affords in good yields the metal-organic framework material $[Ba_3(btc)_2(H_2O)_8]\cdot2H_2O$ (**1**) or the layer compound $[Ca_3(btc)_2(H_2O)_{12}]$ (**2**). The structure of (**1**) is a three-dimensional polymer based on a tribarium building unit. In the trinuclear building block, the central Ba(II) situated on an inversion centre exhibits ten coordination, while the symmetry equivalent terminal Ba(II) ions are eight coordinated. The μ_6-heptadentate bridging binding mode of the unique btc ligand in (**1**) results in a 3-D structure with two water molecules situated in the pores. Compound (**2**) exhibits a two-dimensional structure, unlike the compositionally similar *d*-block compounds $[M_3(btc)_2(H_2O)_{12}]$ (M = Co, Ni, Zn) which are one-dimensional. A comparative study of several compounds containing the $\{M_3(btc)_2\}$ unit is described.

Keywords: Coordination chemistry, Metal-organic framework, Coordination polymers, Barium, Calcium, Trinuclear compounds, Benzene-1,3,5-tricarboxylic acid

The chemistry of metal-organic frameworks (MOFs), also known as coordination polymers (CPs) is currently a frontier area of research. Interest in this field can be evidenced by the publication of special issues of journals on MOF chemistry and several recent review articles[1,2]. In this rapidly developing area of inorganic materials research, different terminologies like metal-organic frameworks, coordination polymers, hybrid inorganic and organic solids, porous coordination polymers, etc., are employed to designate solids with extended structures[2g-2j]. Taking note of this, the inorganic chemistry division of IUPAC has initiated a project to formulate terminology and nomenclature guidelines for CPs and MOFs[3]. In the present work, the term 'framework' is used to designate a barium carboxylate compound which exhibits a three-dimensional (3-D) structure, in accordance with the proposal of Biradha *et al.*[2j]

Most syntheses of extended solids are performed under hydro/solvothermal conditions by combining metal sources with di-, tri-, or tetratopic organic linkers especially carboxylic acids[2d]. Using this principle several metal-organic framework materials have been synthesized and structurally characterized, the most prominent of these being the MOF-5, HKUST-1, MIL-53 (MIL = Materials Institute Lavoisier), MIL-101, etc.[4] In the past two decades *d*-block metals have been extensively employed for the construction of framework materials, while the use of *s*-block metals is comparatively less. Currently, there is a steady growth of papers reporting *s*-block materials and recent developments in this area have been reviewed[2e]. Since the early days of MOF research[2g], the tritopic benzene-1,3,5-tricarboxylic acid (H_3btc) also known as trimesic acid has been the subject of several investigations and has been shown to exhibit several bridging binding modes[5]. Using these connectivities, several extended solids based on btc of varying dimensionalities have been structurally characterized[5-9]. Interestingly a majority of the reported syntheses of alkaline-earth benzene-1,3,5-tricarboxylates have so far been performed under hydrothermal conditions[8]. In this report, we show that a Ba-carboxylate (**1**) and a Ca-carboxylate (**2**), which exhibit 3-D and 2-D connectivities respectively, can be readily assembled under mild reaction (non-hydrothermal) conditions, using H_3btc as an organic linker.

Materials and Methods

All the chemicals used in this study were of reagent grade and were used as received. The starting materials and reaction products are air stable and

hence were prepared under normal laboratory conditions. Infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer in the range 4000-400 cm^{-1}. UV-visible spectra were recorded on a Shimadzu UV-2450 double beam spectrophotometer. Photoluminescence of solid samples were recorded using a Perkin Elmer LS55 fluorescence spectrometer. TG-DTA studies were performed in flowing air in Al_2O_3 crucibles on a STA-409PC simultaneous thermal analyzer from Netzsch, at a heating rate of 10 K min^{-1} for all measurements. Isothermal weight loss studies were performed in a temperature controlled electric furnace. X-ray powder pattern were recorded on a Rigaku Miniflex II powder diffractometer using Cu-Kα radiation with a Ni filter.

Preparation of [Ba$_3$(btc)$_2$(H$_2$O)$_8$].2H$_2$O (1) and [Ca$_3$(btc)$_2$(H$_2$O)$_{12}$] (2)

H$_3$btc (0.42 g, 2 mmol) was dissolved in water (50 mL). To this barium carbonate (0.59 g, 3 mmol) was added slowly under stirring at room temperature. Brisk effervescence was observed during addition of BaCO$_3$ to H$_3$btc solution followed by the immediate separation of compound (**1**) as fine crystals. After 1 h, the fine crystals were filtered, washed well with cold water, followed by alcohol and ether and dried. From the mother liquor colorless crystals of (**1**) suitable for single crystal work were obtained. (Yield = 0.78 g). The use of CaCO$_3$ instead of BaCO$_3$ in the above synthesis afforded colorless crystals of [Ca$_3$(btc)$_2$(H$_2$O)$_{12}$] (**2**) in 80 % yield.

Anal. (%): Calc. for Ba$_3$C$_{18}$H$_{26}$O$_{22}$ (1006.37) (**1**): BaCO$_3$, 58.83; C, 21.48; H, 2.60; Found: BaCO$_3$, 58.12; C, 21.45; H, 2.64. IR data: 3600-3000 (υ_{O-H}), 1697(s), 1614(s), 1549 (s, υ_{as}-COO), 1433 (s, υ_s-COO), 1378 (s), 1284 (s), 1197 (s), 1110 (s), 899 (s), 792 (s), 754 (s), 723 (s), 692 (s), 667 (s), 520 (s) cm^{-1}. DTA data (in ^{o}C): 148 (endo), 525 (exo), 593 (exo). UV-vis (diffused reflectance): 281 nm.

Anal. (%): Calc. for Ca$_3$C$_{18}$H$_{30}$O$_{24}$ (750.65) (**2**): Ca, 16.02; CaO, 22.41; C, 28.80; H, 4.03; Found: Ca, 15.80; CaO, 21.93; C, 30.87; H, 5.22 %; IR data: 3600-3000 (br, υ_{O-H}), 1692 (s), 1607(s), 1549 (s, υ_{as}-COO), 1445 (s), 1433 (s, υ_s-COO), 1390 (s), 1271(s), 1250 (s), 1207 (s), 1111 (s), 930 (s), 856 (s), 795 (s), 762 (s), 729 (s), 687 (s), 529 (s) cm^{-1}. DSC data (in ^{o}C): 131 (endo), 593 (exo), 610 (exo). UV-vis (diffused reflectance): 281 nm.

Dehydration of [Ba$_3$(btc)$_2$(H$_2$O)$_8$].2H$_2$O (1) and [Ca$_3$(btc)$_2$(H$_2$O)$_{12}$] (2)

A weighed amount of compound (**1**) or (**2**) was heated for 1 h at 150 ^{o}C in a temperature controlled oven. This resulted in the formation of the anhydrous compounds [Ba$_3$(btc)$_2$] (**1a**) or [Ca$_3$(btc)$_2$] (**2a**) respectively. The observed mass loss on heating was in good agreement with the expected loss of all water molecules in the starting materials. Equilibration of the anhydrous compounds over water vapour in a dessiccator did not result in any rehydration to form the respective starting compounds.

Anal. (%): Calc. for Ba$_3$C$_{18}$H$_6$O$_{12}$ (826.21) (**1a**): BaCO$_3$, 71.65; Found: BaCO$_3$, 70.21; IR data: 1603 (s), 1543 (s, υ_{as}-COO), 1433 (s, υ_s-COO), 1368 (s), 1207 (s), 1107 (s), 932 (m), 818 (m), 768 (s), 721 (s), 518 (s) cm^{-1}. DTA data (in ^{o}C): 525 (exo), 593(exo). UV-vis (diffused reflectance): 281 nm.

Anal. (%): Calc. for Ca$_3$C$_{18}$H$_6$O$_{12}$ (534.47) (**2a**): CaO, 37.03; Found: CaO, 37.15. IR (KBr) data: 3057 (m), 2983-2486 (br), 1705 (m), 1607 (s), 1555 (s, υ_{as}-COO), 1433 (s, υ_s-COO), 1368 (s), 1109 (s), 984 (s), 772 (s), 710 (s), 532 (s), 460 (m) cm^{-1}. DSC data (in ^{o}C): 593(exo), 610(exo).

X-ray crystal structure determination

Intensity data for (**1**) and (**2**) were collected on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo-Kα radiation. The structures were solved with direct methods using SHELXS-97[10] and refinement was carried out against F^2 using SHELXL-97[10]. All non-hydrogen atoms were refined using anisotropic displacement parameters. C-H hydrogen atoms of the btc ligand were positioned with idealized geometry and refined using a riding model. H atoms attached to the O atoms of water were located in the difference map and were refined isotropically using a riding model. The technical details of data acquisition and some selected refinement results are summarized in Table 1.

Results and Discussion

Synthetic aspects of alkaline-earth btc compounds

Since the first report of a 1:1 Ca-Hbtc compound in 1997 by the Plater group[8a], a total of sixteen alkaline-earth btc compounds have been characterized[8]. The synthesis of all these compounds excepting two Ca compounds[9a,9b] has been performed under hydrothermal conditions (Supplementary Data Table S1). An important requirement of the
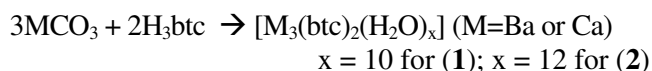
Table 1—Crystal data and structure refinement for
$[Ba_3(btc)_2(H_2O)_8]\cdot 2H_2O$ (**1**) and $[Ca_3(btc)_2(H_2O)_{12}]$ (**2**)

	(**1**)	(**2**)
Emp. formula	$C_{18}H_{26}Ba_3O_{22}$	$C_{18}H_{30}Ca_3O_{24}$
Formula wt (g mol^{-1})	1006.41	750.66
Temp. (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Unit cell dimensions		
a (Å)	12.589(3)	19.288(11)
b (Å)	16.004(3)	11.445(7)
c (Å)	6.8171(14)	12.975(8)
β (º)	91.153(3)	106.317(9)
Vol. (Å^3)	1373(5)	2749(3)
Z	2	4
D_{calc} (mg/m^3)	2.434	1.814
Abs coeff. (mm^{-1})	4.353	0.709
F(000)	956	1560
Crystal size (mm^3)	$0.42 \times 0.19 \times 0.16$	$0.38 \times 0.24 \times 0.22$
θ range for data collect. (º)	1.62 to 25.97	2.09 to 26
Index ranges	$-15 \leq h \leq 15$, $-19 \leq k \leq 19$, $-8 \leq l \leq 8$	$-23 \leq h \leq 18$, $-13 \leq k \leq 14$, $-15 \leq l \leq 15$
Reflections collected	13080	6880
(Rint)	2678 (0.0273)	2666 (0.0200)
Completeness to θ = 28.49º	99.3 %	98.4 %
Refinement method	Full-matrix least-squares on F^2	
Data/ restraints /parameters	2678 / 0 / 237	2666 / 2 / 213
Goodness-of-fit on F^2	1.153	1.056
Final R indices [I >2σ (I)]	R1 = 0.0184, wR2 = 0.0461	R1 = 0.0275, wR2 = 0.0714
R indices (all data)	R1 = 0.0188, wR2 = 0.0463	R1 = 0.0299, wR2 = 0.0729
Largest diff. peak and hole (eÅ^{-3})	0.599 & –0.674	0.264 & –0.355
Bond valence sum of central metal^a	2.072 & 1.946	2.13 & 2.01

Bond valence sums were calculated from crystallographioc data using VaList. A.S. Wills, VaList, program available from www.ccp14.ac.uk

hydrothermal reactions is maintenance of a high reaction temperature for prolonged periods which in some cases is as high as 8 or 10 days as reported for the Be-btc frameworks[8f]. In the present work, synthesis has been performed under non-hydrothermal conditions and the water soluble nature of H_3btc permits a convenient assembly of compounds (**1**) and (**2**) at room temperature. Thus, the reaction of MCO_3 (M = Ba or Ca) with H_3btc in a 3:2 mole ratio in an aqueous medium results in the formation

of (**1**) or (**2**) in good yields, which can be represented as follows:

$$3MCO_3 + 2H_3btc \rightarrow [M_3(btc)_2(H_2O)_x] \text{ (M=Ba or Ca)}$$
$$x = 10 \text{ for } (\mathbf{1}); x = 12 \text{ for } (\mathbf{2})$$

Both compounds can also be prepared by reacting aqueous MCl_2 solutions with *in situ* generated trisodium salt of btc in a 3:2 mole ratio. The high formation tendency of (**1**) or (**2**) can also be evidenced by the fact that both compounds can be prepared by a carboxylate exchange reaction, i.e., by the direct reaction of the alkaline-earth acetate with the aromatic acid. The synthesis of a 1:1 compound[8b] $[Ba(Hbtc)(H_2O)_2]\cdot 0.5H_2O$ and the 3:2 compounds[8i,8j] $[Ba_3(btc)_2(H_2O)_4]\cdot 0.5H_2O$ and $[Ba_3(btc)_2(H_2O)_4]$ containing less coordinated water than (**1**) have been performed under hydrothermal conditions. It is interesting to note that the hemihydrate compound $[Ba_3(btc)_2(H_2O)_4]\cdot 0.5H_2O$ was prepared at a reaction temperature of 170 ºC, while the solvothermal reaction of a mixture of Zn and Ba nitrates in aqueous DMF at 110 ºC has been reported to yield $[Ba_3(btc)_2(H_2O)_4]$ without any incorporation of either the DMF or Zn in the product. In contrast, the use of a mixture of zinc nitrate and $Ca(OH)_2$ in aqueous DMF has been shown to result in the formation of the heterometallic compound $[CaZn_2(btc)_2(H_2O)_2](DMF)_2$ in a solvothermal reaction[8k]. Under hydrothermal conditions the use of Ba- or Ca-acetate as metal source yielded the 1:1 compounds $[M(Hbtc)(H_2O)_2]$ containing the $(Hbtc)^{-2}$ dianion as the linker[8a,b]. It has also been reported that a solvothermal reaction of $Ca(NO_3)_2$ with H_3btc in aqueous DMF in the presence of HCOOH results in the formation of $[Ca_3(btc)_2(H_2O)_2(dmf)_2]\cdot 3H_2O$ in low yield[8d]. The above instances show the differing and unpredictable nature of the products in solvothermal reactions. This can also be evidenced by the fact that the DMF solvent used in the synthesis of the anionic Be frameworks undergoes decomposition providing the dimethylammonium counter cation[8f] while the F$^-$ ion used in the synthesis in the form of HF is not incorporated in the final product given the fact that Be has great affinity for F ligands. Prior to our work, a brief structure report of compound (**2**) prepared by a slow diffusion of NEt_3 (Et = ethyl) into a reaction mixture of $[Ca(acetate)_2]$ and H_3btc in isopropanol-water has appeared[9a]. More recently the synthesis of a 1:1 compound of Ca namely $[Ca(Hbtc)(H_2O)_4]$ has been reported by the reaction of $CaCl_2$ with H_3btc and Na_2CO_3 in aqueous methanolic medium under refluxing conditions[9b].

Spectral and thermal investigations

The characteristic infrared spectra of (**1**) and (**2**) (Supplementary Data Fig. S1), showing no signals in the 1730-1690 cm^{-1} region, serve to demonstrate the formation of a metal:btc compound containing a fully deprotonated btc trianion and the absence of any free –COOH group in the product. The composition of (**1**) and (**2**) was arrived at based on elemental analysis, and thermal and spectral studies. Both compounds which contain metal:btc in a 3:2 ratio are differently hydrated and the metal:water ratio are 3:10 and 3:12 for (**1**) and (**2**) respectively. Compounds (**1**) and (**2**) can be fully dehydrated to the corresponding anhydrous phases, [Ba$_3$(btc)$_2$] (**1a**) and [Ca$_3$(btc)$_2$] (**2a**) respectively by heating at 150 °C. The anhydrous crystalline materials thus formed cannot be rehydrated to the starting materials. The intense O-H vibration observed in (**1**) or (**2**) are not observed in the spectra of (**1a**) and (**2a**), thus confirming the formation of the anhydrous phases (Supplementary Data Fig. S1). The crystalline nature of (**1a**) and (**2a**) can be evidenced by the sharp lines in their X-ray powder pattern (Supplementary Data Fig. S2). A comparison of the powder pattern of (**1a**) with that of (**1**), reveals the differing nature of the starting and the anhydrous material. The thermograms of (**1**) or (**2**) exhibit a first endothermic event (148 ^{o}C for (**1**); 131 ^{o}C for (**2**)) followed by exothermic events above 500 ^{o}C. The endothermic event can be assigned for the dehydration process and has been verified by isothermal weight loss studies by heating (**1**) or (**2**) at 150 ^{o}C. The thermal profile of the anhydrous phases is identical to that of the starting hydrated compounds excepting for the absence of the first endothermic event in (**1**) and (**2**), which accounts for the loss of water molecules (Supplementary Data Fig. S3). The optical spectra of the hydrated and the anhydrous phases are very similar to that of the free ligand indicating that the absorptions are ligand centred (Supplementary Data Fig. S4). Both compounds exhibit diminished fluorescence (Supplementary Data Fig. S4) and the luminescence property can be attributed to ligand centered π or n → π* orbital transitions since similar emissions are also observed for the free ligand.

Structural features

The barium-organic framework compound [Ba$_3$(btc)$_2$(H$_2$O)$_8$]·2H$_2$O (**1**) crystallizes in the centrosymmetric monoclinic space group *P2$_1$/c* and its structure consists of two crystallographically unique Ba(II) ions, an independent trianionic btc ligand and five water molecules (Supplementary Data Fig. S5). The structure of compound (**1**) is polymeric based on a tribarium building block consisting of a central Ba2 linked to two symmetry equivalent Ba1 ions on either side. In the trinuclear unit, Ba2 is situated on an inversion centre and exhibits a coordination number of ten while Ba1 is eight coordinated (Fig. 1). The five water molecules in the crystal structure can be classified into two sets namely four coordinated water molecules (O7 to O10) and an uncoordinated water molecule (O11). The water molecules O7 and O8 are monodentate ligands bonded to Ba1 in a terminal fashion, while O9 and O10 function as μ$_2$-bridging bidentate ligands linking Ba1 with Ba2 (Supplementary Data Fig. S6). The unique btc trianion functions as a μ$_6$-heptadentate bridging ligand and is bonded to six different Ba(II) ions, four of which are Ba1 and two are Ba2 (Fig. 2). Each Ba1 is linked to four different btc units via the oxygen atoms O1, O2, O3 and O6 and to four water molecules O7, O8, O9 and O10, resulting in a distorted square antiprismatic {BaO$_8$} polyhedron (Fig. 3). Like Ba1, the Ba2 situated on a special position is also linked to four different btc ligands via six oxygen atoms O3, O4, O5, O3^i, O4^i and O5^i and to four different water molecules O9, O10, O9^i and O10^i leading to ten coordination (Supplementary Data Fig. S6). The {BaO$_{10}$} polyhedron around Ba2 has a distorted bicapped square antiprismatic geometry. The μ$_6$-heptadentate bridging binding mode of the unique btc ligand in (**1**) results in a three-dimensional structure with the free water molecules (O11) situated in the pores (Fig. 4). The geometric parameters of the organic ligand in (**1**) are in the
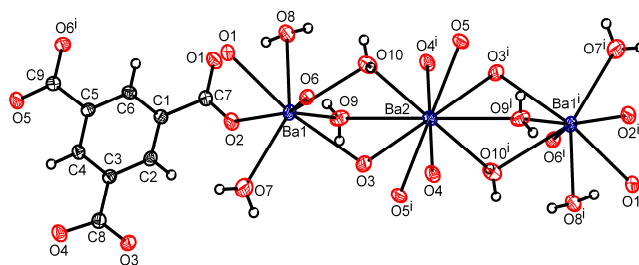

Fig. 1—The basic trinuclear building unit in [Ba$_3$(btc)$_2$(H$_2$O)$_8$]·2H$_2$O (**1**) showing the coordination sphere of the unique Ba(II) ions (Ba1 and Ba2) and the crystallographic labeling scheme. Displacement ellipsoids are drawn at the 50 % probability level except for H atoms, which are shown as circles of arbitrary radius. Symmetry code: (i) -*x*+2, -*y*, -*z*+1.
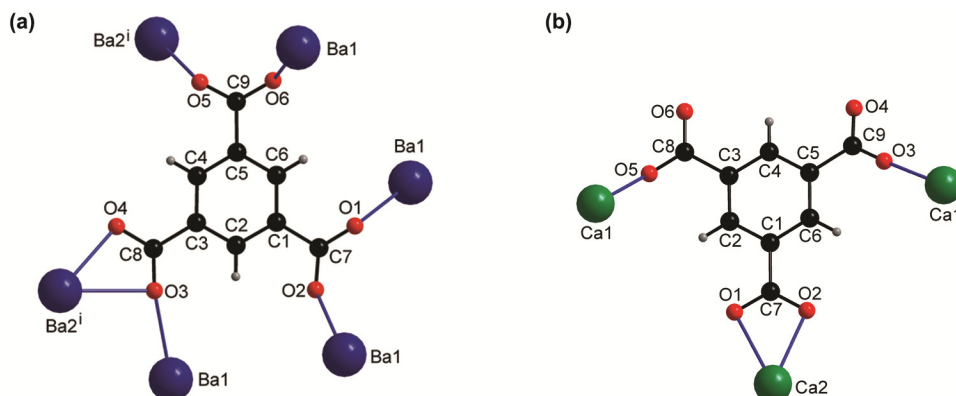
Fig. 2—(a) The μ_6-heptadentate bridging binding mode of the trianionic btc ligand in (**1**) showing its linking to six Ba(II) ions (Ba-O bonds are shown in blue). Symmetry code: (i) -x+2, -y, -z+1. (b) The μ_3-tetradentate bridging binding mode of the trianionic btc ligand in (**2**) showing its linking to three Ca(II) ions (Ca1-O5, Ca1-O3, Ca2-O1 and Ca2-O2 bonds are shown in blue).
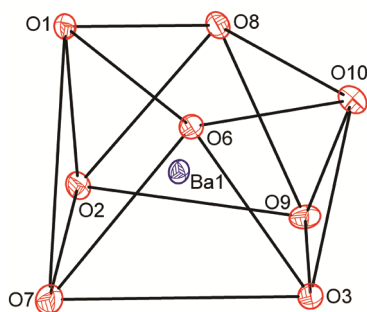

Fig. 3—The distorted square antiprismatic {BaO$_8$} polyhedron around Ba1 in (**1**).

normal range and the O-Ba-O angles scatter in a wide range (Supplementary Data Table S2). The observed Ba-O distances (2.6548(18) to 2.874 Å for Ba1-O; 2.7545(18) to 3.013 Å for Ba2-O) are in good agreement with reported data[8i,8j] for [Ba$_3$(btc)$_2$(H$_2$O)$_4$]·0.5H$_2$O and [Ba$_3$(btc)$_2$(H$_2$O)$_4$]. Compound (**1**) differs considerably from these compounds which contain less number of coordinated water. The compounds [Ba$_3$(btc)$_2$(H$_2$O)$_4$]·0.5H$_2$O and [Ba$_3$(btc)$_2$(H$_2$O)$_4$] which crystallize in the non-centrosymmetric *Pna2$_1$* space group contain three unique Ba ions and two independent btc trianions. The unique btc ligands in these water deficient Ba-btc compounds exhibit a higher denticity (nona or decadentate) and function as μ_7-bridging ligands (Supplementary Data Fig. S7).

Compound (**2**) crystallizes in the centrosymmetric monoclinic space group *C2/c* and the observed unit cell parameters are in agreement with the earlier reported data[9a]. Like in (**1**) the basic building block of compound (**2**) is a trinuclear unit with the central calcium (Ca2) situated on an inversion centre. Unlike in (**1**), both the unique Ca(II) ions Ca1 and Ca2 in (**2**)
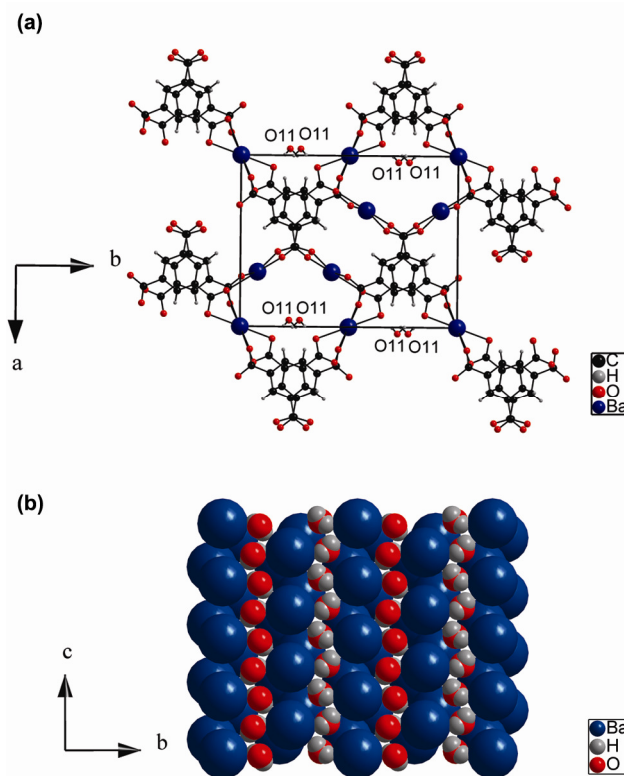

Fig. 4—(a) A view of the unit cell packing of [Ba$_3$(btc)$_2$(H$_2$O)$_8$]·2H$_2$O (**1**) showing the free water molecules (O11) trapped in the pore of the 3-D framework. For clarity, the bridging and terminal waters around Ba1 and Ba2 are not shown. (b) A space filling model of the framework showing only the Ba ions and the trapped water (O11). For clarity, the bridging btc ligands and coordinated waters around Ba are not shown.

are linked to two different btc ligands (Supplementary Data Fig. S8). In (**2**), two of the three –COO groups in the organic linker bind in a monodentate fashion while the third is linked in a bidentate manner resulting in a μ_3-tetradentate btc ligand (Fig. 2). It is

to be noted that none of the three carboxylic group of the unique btc ligand in (**2**) exhibit a bridging binding mode unlike in (**1**). A similar feature is observed in the 1:1 compound[8d] $[Ca(Hbtc)(H_2O)_4]$ where each unique Ca is bonded to four terminal water molecules and each of the three –COO groups in the unique btc ligand functions as a monodentate ligand. In contrast, in the water deficient compound[8d] $[Ca_3(btc)_2(H_2O)_2(DMF)_2] \cdot 3H_2O$, each of the carboxylate groups in the two independent btc ligands exhibit bridging binding modes (Supplementary Data Fig. S9). This indicates that the number of coordinated water molecules around the alkaline earth metal influences the binding mode of the carboxylate ligand.

The geometric parameters of the organic btc ligand are in the normal range and the Ca-O bond distances and O-Ca-O bond angles (Supplementary Data Table S3) are in agreement with reported data[9a]. The H atoms of the coordinated water molecules in both compounds and the uncoordinated water (O11) in (**1**) are involved in several weak H-bonding interactions (Supplementary Data Table S4). In terms of secondary interactions, the framework compound (**1**) differs from the two-dimensional compound (**2**) in that the H4 atom attached to C4 is involved in a weak C-H···O interaction with the lattice water O11.

Coordination behavior of btc ligand towards *s*- and *d*-block metals

The extended solids (**1**) and (**2**) described in this work are members of a group of compounds which contain bivalent metal:btc in a 3:2 ratio. A comparison of several compositionally similar $[M_3(btc)_2(H_2O)_x]$ (M = bivalent metal) compounds reveals the differing coordination behavior of the btc ligand towards *d*- and *s*-block metals. In all these extended solids of differing dimensionalities (Table 2) interesting structural features like (i) varying levels of hydration of the *s*- or *d*-block metal, (ii) different coordination number of the central metal, (iii) varying denticity of the bridging btc ligand, (iv) tendency to crystallize in non-centrosymmetric space groups (Entry 3-5 and 10-16 in Table 2), and, (v) different dimensionality of the extended solid can be observed. The isotypic *d*-block compounds $[M_3(btc)_2(H_2O)_{12}]$ (M = Co, Ni and Zn) are compositionally identical to the Ca compound $[Ca_3(btc)_2(H_2O)_{12}]$ (**2**) and their structure consists of two unique bivalent metal ions and two independent btc ligands, one of which exhibits a μ_3-tetradentate bridging mode as in (**2**). The second unique btc ligand is a μ_2-bridging bidentate ligand and each metal in the trinuclear

unit is bonded to four terminal water molecules thus accounting for the twelve water molecules in the formula unit. Hexacoordination around the *d*-block metal is achieved by bonding to btc ligands (Fig. 5), resulting in the formation of a 1-D corrugated chain structure unlike in $[Ca_3(btc)_2(H_2O)_{12}]$ (**2**) which exhibits a 2-D layer structure. The μ_2-bridging binding mode of one of the water molecules extends the structure of (**2**) in the second dimension and the presence of bridging water molecule enhances the coordination number of the unique Ca ions in (**2**) to 7 and 8 respectively unlike the hexacoordination for the *d* block metals. The twelve water molecules provide a total of fourteen Ca-O(water) bonds, two more than that observed for the *d*-block compounds. In the Ba-organic framework compound (**1**) which contains eight coordinated water molecules, a total of twelve Ba-O(water) linkages are observed, with each Ba in the trinuclear unit bonded to four water molecules. In both compounds (**1**) and (**2**) synthesized under non-hydrothermal (ambient) conditions in aqueous medium, the *s*-block metal is coordinated to four/four (Ba) and five/four (Ca) water molecules per unique metal. Compounds which are synthesized under ambient (non-hydrothermal) conditions in aqueous medium in the absence of other O- or N-donor ligands tend to get maximum hydrated (water-rich) as observed for (**1**) and (**2**). In contrast, the bivalent metal is either anhydrous (Entry 9 and 17) or contains less number of coordinated water molecules per metal (Entry 6-17) in products obtained by (i) hydrothermal synthesis and/ or (ii) use of additional N- or O-donor ligands like py, eg, DMF, dmp, etc., (for abbreviations see Table 2) in the synthetic method. The number of coordinated water ligands around the bivalent metal influences the binding mode of the btc ligand, and has been earlier explained in the case of Ba/Ca-btc compounds. A scrutiny of Table 2 reveals that a reduction in the number of coordinated water molecules (water deficient) leads to an enhanced denticity of the btc ligand. In all the *s*-block compounds, which are synthesized under hydrothermal conditions (Entry 10–14), the btc ligand exhibits both higher denticity and bridging. In the compounds $[Ba_3(btc)_2]$ (**1a**) or $[Ca_3(btc)_2]$ (**2a**) which are devoid of coordinated water molecules, the btc ligands in the formula unit attain an enhanced denticity in order to fulfill the high coordination demands of the alkaline-earth metal, resulting in a reorganization of the structure, which is different from that of the starting water-rich materials

Table 2—Different binding modes of btc ligand in $[M_3(btc)_2(H_2O)_x]$ (M = bivalent metal)

No.	Compound	C. No.	Space group	Binding mode of the independent btc ligands	D	Ref.
1	$[Ba_3(btc)_2(H_2O)_8]\cdot 2H_2O$ (**1**)	8,10 [a]	$P2_1/c$	μ_6-heptadentate	3-D	This work[#]
2	$[Ca_3(btc)_2(H_2O)_{12}]$ (**2**)	7, 8 [a]	$C2/c$	μ_3-tetradentate	2-D	This work[#]
3	$[Co_3(btc)_2(H_2O)_{12}]*$	6, 6 [a]	$C2$	μ_3-tetradentate; μ_2-bidentate	1-D	5b
4	$[Ni_3(btc)_2(H_2O)_{12}]*$	6, 6 [a]	$C2$	μ_3-tetradentate; μ_2-bidentate	1-D	5b, 7b
5	$[Zn_3(btc)_2(H_2O)_{12}]*$	6, 6 [a]	$C2$	μ_3-tetradentate; μ_2-bidentate	1-D	5b, 5d[#]
6	$[Cu_3(btc)_2(H_2O)_3]*$ (HKUST-1)	5	Fm-$3m$	μ_6-hexadentate	3-D	4b
7	$[Cd_3(btc)_2(pipH)(H_2O)_3(OH)]\cdot H_2O*$	6, 6, 6 [b]	$Pbca$	μ_4-tetradentate; μ_5-octadentate	2-D	5e
8	$[Cd_2Co(btc)_2(H_2O)_4]\cdot 2H_2O*$	6, 6, 6 [b]	$C2/c$	μ_5-pentadentate	3-D	5e
9	$[Mn_3(btc)_2]*$	6, 6 [a]	R-3	μ_6-nonadentate	3-D	5f
10	$[Ca_3(btc)_2(H_2O)_2(DMF)_2]\cdot 3H_2O*$	7, 7, 8 [b]	$C2$	μ_6-octadentate; μ_7-nonadentate	3-D	8d
11	$[CaZn_2(btc)_2(H_2O)_2]\cdot(DMF)_2*$	6 (Ca); 4 (Zn)	$C222_1$	μ_6-hexadentate	3-D	8k
12	$[Sr_3(btc)_2(H_2O)_4]\cdot H_2O*$	7, 9, 9 [b]	$Pna2_1$	μ_7-octadentate; μ_7-decadentate	3-D	8c
13	$[Ba_3(btc)_2(H_2O)_4]\cdot 0.5H_2O$ *	7, 9, 9 [b]	$Pna2_1$	μ_7-decadentate; μ_7-decadentate	3-D	8i
14	$[Ba_3(btc)_2(H_2O)_4]*$	7, 8, 9 [b]	$Pna2_1$	μ_7-nonadentate; μ_7-decadentate	3-D	8j
15	$[Ni_3(btc)_2(py)_6(eg)_6]\cdot 3(eg)4H_2O$	6	$P4_332$	μ_3-tridentate	3-D	5g[#]
16	$[Zn_3(btc)_2(DMF)_3(H_2O)]\cdot(DMF)(H_2O)$	5, 5, 6 [b]	$P\,4_12_12$	μ_6-hexadentate; μ_5-hexadentate	3-D	5h[#]
17	$[Zn_3(btc)_2(dmp)_6]\cdot 2.5H_2O$	4,4 [a]	$Pbcn$	μ_2-bidentate	1-D	5d[#]

Abbreviations: C.N. = coordination number; D = dimensionality; a - two crystallographically unique bivalent metals; b - three crystallographically unique bivalent metals; pip = piperazine; DMF = dimethylformamide; py = pyridine; eg = ethylene glycol; dmp = 3,5-dimethylpyrazole; *Compound synthesis performed under hydrothermal conditions; # non-hydrothermal synthesis
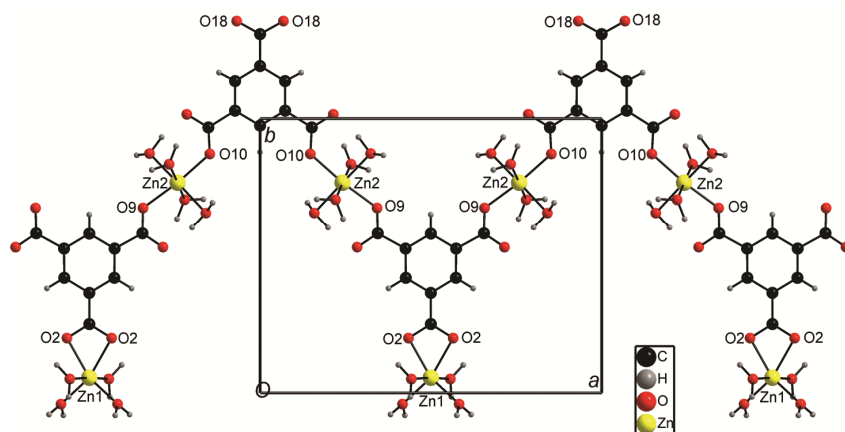

Fig. 5—The corrugated 1-D chain structure of $[M_3(btc)_2(H_2O)_{12}]$ compounds (M = Co, Ni and Zn) due to the μ_3-tetradentate and μ_2-bidentate binding modes of the unique btc ligands. The central metal is hexacoordinated with each metal linked to four terminal H_2O ligands. [Figure drawn for M= Zn using the reported cif data in Ref. 5d].

(**1**) or (**2**). The importance of the coordinated water ligands in (**1**) and (**2**) can thus be evidenced by the fact that on heating at ~150°C both compounds can be fully dehydrated but the anhydrous phases cannot be rehydrated to the original phase indicating the collapse of the original structure.

Conclusions

In summary, we have described the structural characterization of a new barium-organic framework material synthesized under mild reaction conditions. A comparative study of several compounds containing the $\{M_3(btc)_2\}$ unit reveals the versatile ligational behavior of the btc ligand towards *d*- and *s*-block metal ions and that the number of coordinated water molecules around the bivalent metal influences the binding mode of the btc ligands. The Ca-compound $[Ca_3(btc)_2(H_2O)_{12}]$ (**2**) exhibits a two-dimensional structure unlike other compositionally similar *d*-block compounds $[M_3(btc)_2(H_2O)_{12}]$ (M = Co, Ni, Zn), which are one-dimensional.

Supplementary Data

Crystallographic data (excluding structure factors) for the structures of $[Ba_3(btc)_2(H_2O)_8]\cdot 2H_2O$ (**1**) and $[Ca_3(btc)_2(H_2O)_{12}]$ (**2**) reported herein have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 754975 and CCDC 882229. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (Fax: +44-(0)1223-336033 or Email: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article, viz., are available in electronic form at http:\\www.niscair.res.in\jinfo\IJCA\IJCA 51A (08) 1064-1072_Suppl Data.pdf.

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